

Crossover of high and low spin states in transition metal complexes

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Abstract

The stability of high vs. low spin states of transition metal complexes has been interpreted by ligand field theory, which is a perturbation theory of the electron-electron interaction. The present first principles calculation of a series of five cobalt complexes shows that the electron-electron interaction energy difference between the two states (i) exhibits the opposite trend to the total energy difference as the ligand nuclear charge varies, and (ii) is three or four orders of magnitude greater than the total energy difference. A new interpretation of the crossover of high and low spin states is given in terms of the chemical bonding.

Transition metal complexes such as the octahedral CoL_6 exhibit both high and low spin states. The energy difference between these two states $\Delta E = E^{\text{HS}} - E^{\text{LS}}$ depends on the atomic number Z_L of ligand L; the high spin state of E^{HS} is stable for large Z_L and low spin state of E^{LS} for small Z_L . For almost a century, this crossover has been interpreted by ligand field theory which is a perturbation theory ascribing ΔE to the electron–electron repulsion energy difference $\Delta V_{ee} = V_{ee}^{\text{HS}} - V_{ee}^{\text{LS}}$ between the two states [1–5]. Our quantum chemical calculation of a series of CoL_6 complexes, however, shows that, ligand field theory and any other attempts to ascribe ΔE to ΔV_{ee} are invalid, because ΔV_{ee} (i) never changes sign, (ii) decreases with decreasing Z_L and thus exhibits the opposite trend to ΔE , and (iii) is three or four orders of magnitude greater than ΔE , clearly beyond perturbation theory. Correctly, the spin multiplicity is variationally determined by an intricate interplay between the electron–electron repulsion V_{ee} , the electro-nuclear attraction V_{ne} , and the nucleus–nucleus repulsion V_{nn} . In conclusion, the crossover of high and low spin states is a consequence of different Co–L bondings, ionic or covalent, which is found by an accurate treatment of Coulomb correlation between ligand p and cobalt d electrons in the present calculation.

Quantum chemical first principles calculations were carried out using the GAMESS [6] package. Coulomb correlation is included via the complete active space self-consistent field (CAS-SCF) method, where full configuration interaction calculations are carried out within the chosen active spaces. Our active spaces are chosen from the transition atom $3d$, $4d$ and ligand $2p$ orbitals [CAS(12,10)]; in CAS(10,6) the ligand $2p$ orbitals are excluded. For each complex and spin state, the molecular geometry is fully optimized. All calculations satisfy the virial theorem $2T + V = 0$ with the virial ratio $V/T = -2.000 \pm 0.001$. For F in $[\text{CoF}_6]^{3-}$ and N in $[\text{Co}(\text{CN})_6]^{3-}$ we use the basis set 6-31G^{++*}, and 6-31G^{**} for all other atoms.

We study five octahedral cobalt complexes: $[\text{CoF}_6]^{3-}$, $[\text{Co}(\text{OH}_2)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Co}(\text{CO})_6]^{3+}$. The first two have quintet ($S = 2$; high spin) ground states, and the remaining three singlet ($S = 0$; low spin) ground states. [7–9] The calculated energy differences $\Delta E = E^5 - E^1$ between the quintet and singlet states for the five complexes are given in table I. Obviously, the singlet ground states of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Co}(\text{CO})_6]^{3+}$ are predicted correctly only if Coulomb correlation is considered for those ligand L p electrons which form σ bonds with the central cobalt atom as well as for the Co d electrons [CAS(12,10)]; the inclusion of Coulomb correlation only for the Co d electrons [CAS(10,6)] leads to wrong ground states.

TABLE I: Energy difference ΔE between high and low-spin states in Hartree atomic units, evaluated in Hartree-Fock (HF) and complete active space self-consistent field [CAS(12,10) and CAS(10,6)] calculations.

Complex	HF	CAS(10,6)	CAS(12,10)
$[\text{CoF}_6]^{3-}$	-0.11	-0.08	-0.05
$[\text{Co}(\text{OH}_2)_6]^{3+}$	-0.09	-0.06	-0.03
$[\text{Co}(\text{NH}_3)_6]^{3+}$	-0.06	-0.03	0.01
$[\text{Co}(\text{CN})_6]^{3-}$	-0.04	-0.01	0.05
$[\text{Co}(\text{CO})_6]^{3+}$	-0.06	-0.03	0.02

The energy differences ΔE (table I) are as small as some tens of milliHartree, while the total energies are as large as 2000 Hartree per complex. Earlier studies of high and low spin states have relied on perturbation theory [1–5, 10–13] instead of calculating ΔE from the total energies $E^{2S+1} = T^{2S+1} + V_{ne}^{2S+1} + V_{nn}^{2S+1} + V_{ee}^{2S+1}$ for each S . These earlier studies are based on the assumption that $T^{2S+1} + V_{ne}^{2S+1} + V_{nn}^{2S+1}$ has no dependence on the spin multiplicity $2S + 1$, and that ΔE can be ascribed solely to V_{ee}^{2S+1} , i.e. $\Delta E \approx \Delta V_{ee}$. In this work, the potential energy difference and its components ΔV ($= \Delta V_{ee} + \Delta V_{ne} + \Delta V_{nn}$) given in table II are calculated under the virial theorem condition $E^{2S+1} = \frac{1}{2}V^{2S+1} = \frac{1}{2}(V_{ne}^{2S+1} + V_{nn}^{2S+1} + V_{ee}^{2S+1})$, satisfying the virial ratio $V^{2S+1}/T^{2S+1} = -2.000 \pm 0.001$ up to at least three digits for both the high and low spin states. We find that the leading contribution to ΔE is not ΔV_{ee} but ΔV_{ne} that comes from the difference in the electron density distribution between the two states. ΔV_{ne} is the only energy difference component that exhibits an increasing trend with decreasing Z_L in a similar way as ΔE ; ΔV_{ee} and ΔV_{nn} exhibit the opposite trend. However, none of ΔV_{ee} , ΔV_{nn} , and ΔV_{ne} individually changes sign with decreasing Z_L , and each of them is three or four orders larger than ΔE in magnitude. Thus, the crossover of high and low spin states is the outcome of a delicate interplay of all three potential energy components.

In order to clarify why the ground state varies from high to low spin states, we give a detailed analysis of the potential energy V and its components V_{ee} , V_{nn} , and V_{ne} . We calculate E^{2S+1} by both Hartree-Fock (HF) and complete active space self-consistent field (CAS-SCF) methods. Electrons tend to avoid each other due to Pauli’s exclusion principle

TABLE II: Potential contributions ΔV_{ee} , ΔV_{nn} , and ΔV_{ne} to the energy difference ΔE in Hartree atomic units evaluated in HF and CAS(12,10) calculations.

Complex		ΔV_{ee}	ΔV_{nn}	ΔV_{ne}
$[\text{CoF}_6]^{3-}$	HF	-27.47	-24.37	51.48
	CAS(12,10)	-27.48	-23.5	50.84
$[\text{Co}(\text{OH}_2)_6]^{3+}$	HF	-31.76	-30.54	62.01
	CAS(12,10)	-33.31	-31.23	64.31
$[\text{Co}(\text{NH}_3)_6]^{3+}$	HF	-37.02	-35.08	71.95
	CAS(12,10)	-38.81	-36.29	75.21
$[\text{Co}(\text{CN})_6]^{3-}$	HF	-54.42	-49.72	103.95
	CAS(12,10)	-69.27	-64.19	133.51
$[\text{Co}(\text{CO})_6]^{3+}$	HF	-58.58	-57.59	115.98
	CAS(12,10)	-72.34	-71.69	144.07

(Fermi correlation) and due to Coulomb repulsion (Coulomb correlation). Fermi correlation is already accounted for in HF and is strongest when the number of spin-parallel electrons is largest. On the other hand, Coulomb correlation is strongest when the number of spin-parallel electrons is smallest and hence causes the crossover of high and low spin states. Coulomb correlation not only reduces the short-range interelectronic contribution of V_{ee} , but also affects V_{ne} and V_{nn} . [14–17] Coulomb correlation gives rise to the Coulomb hole between spin-antiparallel electrons and at the same time deepens the Fermi hole between spin-parallel electrons. These correlation holes have an effect to reduce the Hartree-Fock screening of the nuclei at short interelectronic distances, leading to a contraction of the electron density distribution around individual nuclei as well as to a change in the equilibrium nuclear configuration. The correlation effects on V_{ee} , V_{nn} , and V_{ne} are described in the following.

The potential energy difference ΔV_{nn} between high and low spin states arises from a change in the equilibrium nuclear configuration $\{\vec{R}_I\}$. As is seen from table III, the bond lengths between the central cobalt atom and the six ligands are always larger for the quintet state and hence $V_{nn}^5 < V_{nn}^1$. It means that the high spin state complexes are larger in size than the low spin state ones. Therefore, the average value of the electron–electron separation

TABLE III: Equilibrium Co–L bond lengths in Bohr atomic units for high and low spin states (HS and LS) evaluated in HF and CAS(12,10) calculations. Where two values are given, the z bond is shorter and the x and y bonds are equally long. Where three values are given, the x , y and z bonds are inequivalent.

Complex	HF	CAS(12,10)
$[\text{CoF}_6]^{3-}$	LS 3.592	3.592
	HS 3.623, 3.795	3.621, 3.789
$[\text{Co}(\text{OH}_2)_6]^{3+}$	LS 3.634	3.621
	HS 3.812	3.800
$[\text{Co}(\text{NH}_3)_6]^{3+}$	LS 3.853	3.838
	HS 4.052, 4.116	4.078, 4.086, 4.097
$[\text{Co}(\text{CN})_6]^{3-}$	LS 3.878	3.766
	HS 4.144, 4.225	4.137, 4.188
$[\text{Co}(\text{CO})_6]^{3+}$	LS 3.946	3.840
	HS 4.269, 4.309	4.263

$|\vec{r}_i - \vec{r}_j|$ is enlarged for the high spin state complexes, i.e. $V_{ee}^5 < V_{ee}^1$. Similarly, the average value of the electron–nucleus distances $|\vec{R}_I - \vec{r}_j|$ tends to be reduced in the low spin state complexes, i.e. $V_{ne}^5 > V_{ne}^1$. This trend is observed for both HF and CAS-SCF and explains why the repulsive V_{ee} and V_{nn} favor high spin states and the electron–nucleus attraction low spin states. Next we examine which effect causes the change in sign of ΔE , i.e. the crossover of high and low spin states for $Z_L < 8$.

For complexes with $Z_L \geq 8$, the sum of ΔV_{nn} and ΔV_{ee} is greater than ΔV_{ne} because Fermi correlation that tends to maximize the spin multiplicity [15] dominates over Coulomb correlation. As Z_L becomes smaller than 8, the Coulomb correlation effects become larger and larger, especially for ΔV_{ne} , which overwhelms the sum of ΔV_{nn} and ΔV_{ee} . We find that this remarkable increase in ΔV_{ne} is due to a change in the nature of the chemical bond: the bonding σ orbitals are ionic for $Z_L \geq 8$ and covalent $Z_L < 8$. In Fig. 1 we show the radial distribution $D(r)$ of these σ orbitals. There is a striking difference between the complexes with $Z_L \geq 8$ and $Z_L < 8$. $D(r)$ for the complexes with $Z_L < 8$ exhibits a maximum close to the central cobalt, followed by a minimum around the bond center, and an increase towards

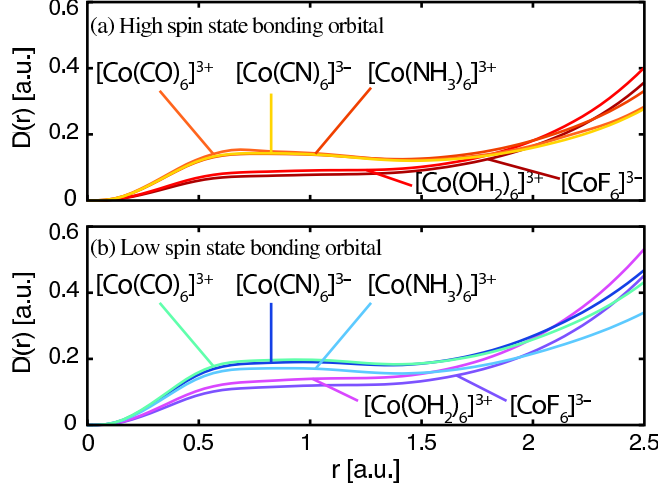


FIG. 1: Charge density distribution $D(r)$ of bonding orbitals for each complex in Hartree atomic units obtained in HF calculation. (a) High spin states. (b) Low spin states.

another maximum close to the ligand. This two-hump shape is a typical example of the charge density distribution in the covalent bond. On the other hand, $D(r)$ of the fluorine and water complexes only has one maximum close to the ligand, and monotonously decreases towards the cobalt atom, typical of the ionic bond. This terminology of ionic and covalent bonds is consistent with Pauling's description of the very same complexes, [8, 9] but the fact that covalent complexes tend to exhibit low spin states and ionic complexes high spin states still remains undescribed. We unveil this mechanism in the following:

Let us illustrate the central transition atom T and the octahedral ligand L_6 as two potential boxes (Fig. 2). The covalent complex is depicted as a set of two connected boxes, and the ionic complex as two separated boxes, which are filled up to the same electron chemical potential. This illustration represents the qualitative differences in the nature of the σ orbitals (Fig. 1), which yield qualitatively different Coulomb correlation effects. Coulomb correlation enhances electron localization, which is depicted as a deepening of the boxes. For the covalent complex, the T and L_6 boxes are both deepened, while for the ionic complex, only the L_6 box is deepened, corresponding to whether the σ orbital distribution (Fig. 1) has two maxima or one. Since for the ionic complex the main Coulomb correlation effect occurs in the ligands, the central transition atom essentially behaves as an isolated atom or ion, where the highest spin multiplicity state has the lowest energy due to Fermi correlation. [15] On the other hand, for the covalent complex, also the T box becomes

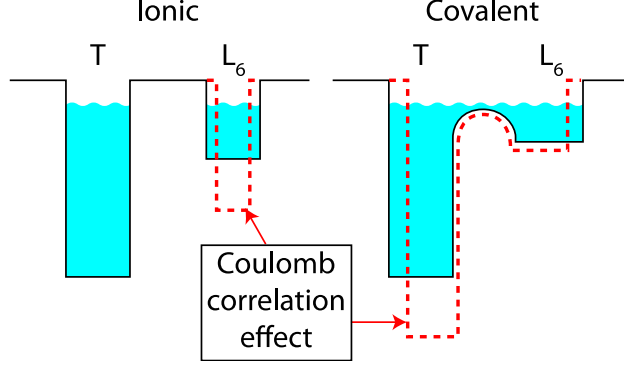


FIG. 2: Potential box illustration of ionic and covalent complexes. Both the transition metal T and ligand L_6 potential boxes are filled up to the same electron chemical potential. The solid black line illustrates the HF calculation, and the red dashed line illustrates the deepening of the potential boxes due to Coulomb correlation included via CAS(12,10). The internuclear distance between T and L_6 is widened for Ionic and reduced for Covalent by the action of correlation.

deeper and moreover this deepening is larger at T than at L_6 . This is because the attractive potential due to nucleus I , $V_{ne,I} = -\sum_j Z_I/|\vec{R}_I - \vec{r}_j|$, is proportional to the nuclear charge Z_I , and hence an enhancement in electron localization at T yields a larger energy gain than it would at L_6 , because $Z_T > Z_L$. Therefore, only for the covalent complex, the electronic configuration of the central transition atom T is strongly influenced by the spin-paired σ bonding orbitals formed mostly of ligand p electrons and hence the low spin state is the ground state.

Our calculations show that octahedral cobalt ($Z_{Co} = 27$) complexes with ligands of $Z_L < 8$ exhibit low spin states in accordance with experiment. The energy gain that stabilizes the low spin states of these cobalt complexes arises from Coulomb correlation effects in the covalent Co-L bonding that lowers $V_{ne,Co} = -\sum_j Z_{Co}/|\vec{R}_{Co} - \vec{r}_j|$. Obviously, this energy gain is expected to be smaller for lighter transition atoms because of the proportionality $V_{ne,I} \propto Z_I$. Indeed, octahedral complexes of iron ($Z_{Fe} = 26$) with the ligand $Z_L < 7$ exhibit low spin states. The crossover of high and low spin states is accompanied with a change from ionic to covalent bonding. We have demonstrated that the electron density distribution and the equilibrium nuclear configuration are strikingly different between the ionic and covalent bondings. These differences are accompanied with changes in V_{ne} and V_{nn} , which are as significant as changes in V_{ee} . To conclude, theories relying on V_{ee} alone predict

wrong ground states, so earlier works [1–5, 10–13] together with any textbook description of high and low spin states neglecting V_{ne} and V_{nn} are invalid.

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